IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant: LIU et al.

Title: SYSTEMS AND METHODS FOR PRODUCING SINGLE-WALLED CARBON NANOTUBES (SWNTS) ON A SUBSTRATE

Appl. No.: 10/759,592

Filing Date: 1/16/2004

Examiner: D. Miller

Art Unit: 1775

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RULE 132 DECLARATION

I, Richard Czerw, declare and say as follows:

1. I submit this declaration in support of the above-identified application for a U.S. patent.

2. I am currently employed as President of NanoTechLabs, Inc (NTL), a North Carolina nanomaterials company that I founded in 2004. NTL produces organic and inorganic nanomaterials used in both the defense and biotech industries. NTL's product development efforts include a conductive, metal free elastomers, thermosets, and thermoplastics. I have 10 years of experience in the synthesis and application of carbon nanotubes and other nanostructures and over 40 published refereed journal articles in nanotechnology and carbon nanotube growth, including "Advances in CNX growth," Liu et al. Mat. Res. Soc. Symp. Proc. Vol. 772 (2003). and "N-doping and coalescence of carbon nanotubes: synthesis and electronic properties," Appl. Phys. A 74, 355–361 (2002) that describe a floating catalyst nanotube growth method similar to that described by Zhu et al. infra.

I was previously employed as a research scientist at Wake Forest University, Winston-Salem, NC and as the engineering manager for Athens Corp., a semiconductor equipment manufacturer in Oceanside, CA. I also served in the U.S. Navy for eight years as a reactor operator on fast attack submarines. My Ph.D. degree is in Physics from Wake Forest University and I was awarded a B.S. degree in Physics from Clemson University.

3. I was informed that the above-identified patent application has been licensed by the interest of Duke University to Unidym, Inc., a majority-owned subsidiary of Arrowhead Research Corporation.

4. I have a collaboration with Carbon Nanotechnologies Inc. (CNI) which was recently acquired by Unidym. My collaboration with CNI is in the conductive composites area and was established several years prior to CNI's acquisition by Unidym.

5. In preparing this declaration, I have reviewed the Zhu et al. reference (Science 3 May 2002 Vol. 296).

6. I do not believe that the Zhu et al. reference teaches an individual single-walled carbon nanotube (SWNT) synthesized on a substrate, wherein the nanotube has a length of at least 1 mm from one end to an opposite end of the individual nanotube.

7. I do not believe that the SWNT strands described by Zhu et al. contain SWNTs that run continuously for a millimeter, let alone a centimeter. My reasons are as follows:

8. First, there is no evidence of long individual SWNTs in the description provided in Zhu et al. On page 884, second paragraph of the article, Zhu states "in which large portions of long SWNTs are formed and assembled into macroscopic strands." This is the only mention of long SWNTs comprising the strands and no estimate of length is given nor does any of the microscopy shown indicate length of individual tubes. Typical SWNT length is only about 0.1 to 5 microns, and "long" could be any length greater than these usual micron lengths. Also, it is extremely difficult to determine accurate lengths of SWNTs because of their small diameters (typically 1 nm as stated in Zhu) and their propensity to bundle due to van der Waals attraction. No evidence is given in the article that any attempts were made to isolate and assess the length of the SWNTs, nor is any high resolution microscopy shown that makes

this determination possible by the reader. Throughout the rest of the article, Zhu refers only to nanotube strands which are bundles of SWNTs, and it is the strand length, not the individual tube lengths, that reaches cm lengths.

9. Second, a vertical furnace was used for synthesis and claims are made of a continuous production method. From my experience with this type of thiophene growth, the catalysts do not affix to the sides of the reactor tube but "float" on the gas stream. The "as grown" material flows down the vertical tube and can be removed at the bottom. Typically, based on the low gas flow rates of 250 ml/min of H_2 given in the paper, and the low injection rates of 0.5 ml/min, the reactor tube diameter would be 1" or 2". Larger diameters could be used, but these are expensive in terms of quartz cost and furnace cost and are not indicated by the growth parameters given in the paper. Most academics that I am familiar with do not use larger tube diameters because of cost and the difficulty in operating larger (length, diameter) furnaces. Assuming a 2" diameter tube, 36" long heated zone furnace (typical for this type of CVD), and using the given mass flow rate and the ideal gas law to estimate the expansion of the gas from 30°C to 1000°C, a total resonance time of the gas, and hence the total growth time of the nanotubes, can be estimated to be less than 2 minutes. This is significant since nanotube growth rates in the literature range from about 0.18 μm/s (A.A. Puretzky et al. "In situ measurements and modeling of carbon nanotube array growth kinetics during chemical vapor deposition," Appl. Phys. A 81, 223–240 (2005)) to ~4 μm/s (Kenji Hata et al. "Water-Assisted Highly Efficient Synthesis of Impurity-Free Single-Walled Carbon Nanotubes," Science 306 pp 162-1364 (2004)). From our own growth of long nanotubes, we estimate the rate to be close to that derived by Yun et al. (YeoHeung Yun, Vesselin Shanov, Yi Tu, Srinivas Subramaniam, and Mark J. Schulz "Growth Mechanism of Long Aligned Multiwall Carbon Nanotube Arrays by Water-Assisted Chemical Vapor Deposition," J. Phys. Chem. B 2006, 110, 23920-23925) of 0.8 μm/s.

If we use 1.0 μm/s as an average growth rate, the nanotubes grown by Zhu would be less than about one hundred μm due to the short resonance time (< 2 min) in the furnace. Even if one assumes that some of the nanotubes are "snagged" by the tube walls and remain longer in the growth zone, we found, after the filing date of US App. No. 10/759,592, that it takes extreme stability in growth parameters (temperature, gas flow, carbon pressures, etc.) to grow mm or

cm over several hours and this is probably not achieved in the Zhu process as described (see Yun et al. mentioned above for stable growth condition requirements).

10. Third, the temperature dependence of the resistance in continuous SWNT strands should not exhibit an upturn at 90 K as the temperature is reduced, as reported by Zhu et al. (page 884, col. 3). This upturn is a signature of the conduction mechanism being one involving tube-to-tube hopping, implying that the conduction paths require that electrons hop across tube-tube junctions (in a phonon assisted process) to get from one end of the fiber to the other.

11. Fourth, the Young's modulus of hexagonally close packed (10, 10) SWNTs should be ~650 GPa. Since Zhu et al. report a density of 48%, and the modulus scales with the cross-sectional area occupied, the corresponding Young's modulus should be 312 GPa for continuous SWNT strands. However, Zhu et al. claim a Young's modulus of 49 to 77 GPa—at best only a fraction of what they should have if the nanotubes in the strand ran the entire length of the fiber (page 884, col. 3).

12. Fifth, there is a quite natural mechanism for forming such strands, wherein catalyst particles deposited at the tips of SWNTs in the strand nucleate new SWNTs, rather than continuing growth of the SWNTs to which they are originally attached.

13. I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true, and further that these statements were made with the knowledge that willful, false statements and the like so made are punishable by fine or imprisonment or both, under Section 1001 of Title XVIII of the United States Code and that such willful, false statements may jeopardize the validity of the above-identified application or any patent resulting there from.

By _____

Richard Czerw, Ph.D.

Date: 11/30/07